DATE: January 5, 2006 FILE REF:

TO: Eileen Pierce – AM/7

Jon Heinrich – AM/7 Ed Miller - SER

FROM: Mark K. Allen – AM/7

David Grande - AM/7

SUBJECT: 2006 Statewide Urban Air Toxic Monitoring Plan

1. Monitoring Objectives

Urban Air Toxics Monitoring (UATM) will be conducted to obtain information on ambient concentrations of volatile organic compounds (VOCs), semi-volatile organic compounds, and non-volatile metals that are hazardous to human health. This program incorporates six monitoring stations located throughout Wisconsin. While most of the UATM monitoring is conducted in urban areas, Wisconsin's program does include some monitoring at remote locations to establish background concentrations of selected pollutants. The compound species to be collected and monitored are listed in Table 3 (attached). Please be sure to note that not all parameters are analyzed year round.

2. General Considerations

a. Siting Sample collection for all parameters will be conducted at the UATM sites listed below;

| Table 1: UATM Monitoring Sites | | | | | | | | | |
|--------------------------------|------------------|-------------|-------------|-------|-------------|-------------|-------|--|--|
| City | Site Name | AIRS# | VOCs | Carbs | PCBs | Metals | NH3 | | |
| Madison ¹ | East High | 55-025-0041 | X | X | | X (as TSP) | | | |
| Mayville | Mayville | 55-027-0007 | X | X | | X (as PM10) | X^2 | | |
| Milwaukee | Sixteenth Street | 55-079-0010 | X | X | X | X (as TSP) | | | |
| Crandon | Potawatomi | 55-041-0007 | | | | X (as TSP) | | | |

^{1.} The Madison site restarted operations in September 2004. This site is part Regional AT network. Samples are analyzed at ERG.



^{2.} Ammonia monitoring is conducted on coated denuders. Analysis is conducted at the ISWS

| Table 2:Sampling Schedule for Statewide Urban Air Toxics ¹ | | | | | | |
|---|---|----------------------|--|--|--|--|
| Monitoring Parameters | January 5, 2006 to December 31, 2006 | Sampling Period | | | | |
| VOCs and Carbonyls | 1/6 (Mayville & Madison) 1/12 days (Milwaukee) | 24-hours | | | | |
| PCBs (semi-volatiles) | 1/12 days | 72-Hour ² | | | | |
| Metals (non-volatiles) | 1/6 (Mayville) 1/12 (Madison) 1/30 days (other sites) | 24-Hour | | | | |
| Hexavalent Chromium | 1/6 (Mayville) | 24-Hour | | | | |

¹ – For operating simplicity and to conform to the national sampling program, the sampling schedule will follow the same schedule dates that are used by the particulate network.

c. Operations

Mark Allen will serve as the overall Project Manager for UATM monitoring and will provide general assistance in all areas of the monitoring project; David Grande will assist in this effort.

i. Task #1 - Sample Collection

Darlene Luehring and Michael Olson will be responsible for the collection of samples at the Mayville site. This will include the collection of quality control samples (blanks, duplicates, collocates and spikes).

Southeast Regional Monitoring staff will be responsible for the collection of samples from Sixteenth Street sites. This will include the collection of quality control samples (blanks, duplicates, collocates and spikes).

David Grande will serve as liaison chemist for all sites and will take the lead in seeing that this task is accomplished. In addition, he will be responsible for the preparation of PS-1 sampling heads for sampling and ensuring they are available to the operators prior to sampling.

ii. Task #2 - WDNR/Laboratory Coordination

David Grande will be responsible for the coordination of samples between the laboratory and the field. Mark Allen will assist David.

David Grande and Mark Allen will responsible for resolving technical questions on sampling and analysis.

iii. Task #3 - Canister analysis

The SLOH Environmental Sciences Section will analyze whole air samples, collected in canisters, for air toxics by gas chromatography/mass

²- All sampling periods are 72-hours.

spectrometry.

iv. Task #4 - Cartridge analysis

The SLOH - Occupational Health Laboratory will analyze exposed DNPH coated cartridges for carbonyl species using high performance liquid chromatography (HPLC).

v. Task #5 - Semi-volatile Compound analysis

The SLOH - Environmental Sciences Section will analyze PS-1 filters and polyurethane foam plugs (PUFs) for polychlorinated biphenyl species and pesticides using high performance gas chromatography with electron capture detection (GC/ECD). Mass spectroscopy may also be employed for compound confirmation.

vi. Task #5 - Non-volatile Metals analysis

The SLOH - Environmental Sciences Section will analyze TSP and PM10 filters for metals using inductively couple plasma mass spectrometry (ICP-MS).

ERG Laboratory in N.C. will analyze filters for hexavalent chromium using a modified CARB methodology.

vii. Task #6 - Quality Assurance

Steve Schuenemann and Mark Allen will be responsible for QA activities on the monitoring project. These activities will include; Sampling and analysis QC objectives as outlined in Quality Assurance Project Plan; and QA activities developed to support the monitoring efforts.

David Grande will be responsible for conducting and reporting on internal performance audits (zero audits) at VOC and carbonyl monitoring stations. This will include checks of air sampling rates.

viii. Task #7 - Data Management

Mark Allen will provide overall responsibility for the management of data collected on the UATM network. Data Unit will assist Mark.

ix. Task #8 - Data Analysis and Reporting

David Grande and Mark Allen will be responsible for the preliminary data analysis and for writing the final program report.

x. Task #9 - Training

David Grande will coordinate training of the site operators for the program. David will also update and revise the present Standard Operating Procedures.

3. Monitoring Plan Specifics

a. Quality Assurance

Quality assurance objectives, activities and goals for 2000 UATM program will be conducted according to *QA.8.0 Hazardous Air Contaminants Urban Monitoring Program*. A copy of the plan has been included in the UATM handbook.

b. Sample Collection Operating Procedures

Sample collection will be conducted according to the following SOPs from the Wisconsin Air Monitoring Handbook:

OP.1.2. High Volume Sampler;

OP.8.5 PS-1 Sampler for Semi-volatile Organic Compounds; and OP.11.0 The Automated Combination Cartridge and Canister Sampler

c. Sample Analysis

Sample analyses will be conducted using the SLH and OHL protocols. These protocols follow the general guidance provided in the following methods:

Method TO-14A - Determination Of Volatile Organic Compounds (VOCs) In Ambient Air Using Specially Prepared Canisters With Subsequent Analysis By Gas Chromatography

Method TO-11A: Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC)

Method IO-3.4: Determination of Metals Captured on Glass Fiber Filter and Analyzed by Inductively Coupled Plasma (ICP) Spectrometry

d. Sampling Schedule

The sampling schedule for the project is given in Table 4(a), 4(b) and 4(c).

e. Data Management

Many samplers used at the monitoring sites automatically collect the sampling field data. This sampling data will be routinely downloaded over phone lines to the AMPAMS fileservice on the CENTRAL. After editing sampling field data will be downloaded to the WISARDS data system. Laboratory data will be electronically transferred through the DNR's laboratory portal to the WISRADS data system. An adjunct repository of all laboratory and field data will be an ACCESS file on AMPAMS file service of CENTRAL.

The final repository of the laboratory and field data will be in the centrally located WISARDS Database. After being reviewed data will be processed by WISARDS for submission to the EPA's AQS database.

All supporting meteorological monitoring data will be collected and managed by the Central Office Data subunit and the Southeast Regional Data staff using WISARDS.

cc: Ron Arneson - TS/6 Natalene Cummings - FCP

Jeff Myers - AM/7 Darlene Luehring - Horicon Service Center

Air Monitoring Staff

Steve Geis – SLOH

Terry Burke - WOHL

John Strauss – SLOH

Mike Koerber - LADCO

Chris Worley – SLOH Motria Caudill - USEPA, Region 5

Attachments

| TABLE 3:UATM Target Vola | tile Organic Com | pounds | |
|--------------------------------|------------------|--------------------------|--|
| Table 3a. Non Polar Volatile C | | | |
| 1,1,1-trichloroethane | 71-55-6 | Chloroprene | 126-99-8 |
| 1,1,2,2-tetrachloroethane | 79-34-5 | c-1,3-dichloropropene | 542-75-6 |
| 1,1,2-trichloroethane | 79-00-5 | Dibromochloromethane | 124-48-1 |
| 1,1 dichloroethane | 75-34-3 | Ethylbenzene | 100-41-4 |
| 1,2 dichloroethane | 107-6-2 | Ethylene dichloride | 107-06-2 |
| 1,2-dichlorobenzene | 95-50-1 | Methyl chloride | 74-87-3 |
| 1,2-dichloropropane | 78-87-5 | Methylene chloride | 75-09-2 |
| 1,3-butadiene | 106-99-0 | Propene | 115-07-1 |
| 1,3-dichlorobenzene | 54-17-3 | M-xylene | 1330-20- 7 |
| 1,4-dichlorobenzene | 106-46-7 | n-octane | 111-65-9 |
| Acetylene | 74-86-2 | O-xylene | 1330-20- 7 |
| Benzene | 71-43-2 | p-xylene | 1330-20- 7 |
| Bromodichloromethane | 75-27-4 | Styrene | 100-42-5 |
| Bromoform | 75-25-2 | Tetrachloroethene | 127-18-4 |
| Bromomethane | 74-83-9 | Toluene | 108-88-3 |
| Carbon tetrachloride | 56-23-5 | Trichloroethene | 79-01-6 |
| Chlorobenzene | 108-90-7 | t-1,2-dichloroethene | 540-59-0 |
| Chloroethane | 75-00-3 | t-1,3-dichloropropene | 542-75-6 |
| Chloroform | 67-66-3 | Vinyl chloride | 75-01-4 |
| Table 3b. Polar Volatile Organ | nic Compounds | | 1 |
| Formaldehyde | 50-0-0 | Valeraldehyde | 110-62-3 |
| Acetaldehyde | 75-07-0 | Isovaleraldehyde | 590-86-3 |
| Acetone | 67-64-1 | Hexaldehyde | 66-25-1 |
| Propionaldehyde | 123-38-6 | Benzaldehyde | 100-52-7 |
| Butyraldehyde | 123-72-8 | M/P- Tolualdehyde | |
| 2-Butanone | 78-93-3 | O-Tolualdehyde | 529-20-4 |
| Crotonaldehyde | 123-73-9 | 2,5-Dimethylbenzaldehyde | 5779-94-2 |
| Table 3c. Semi-volatile Organi | ic Compounds | | |
| Total PCBs as Arochlors | 1336-36-3 | Atrazine | 1912-24-9 |
| Table 3d. Non-volatile Metals | | | |
| Lead | 7439-92-1 | Manganese | 7739-96-5 |
| Arsenic | 7740-38-2 | Nickel* | 7440-02-0 |
| Cadmium | 7440-43-9 | Beryllium* | 7440-41-7 |
| Chromium - total & Cr(VI) | 7440-47-3 | * - Mayville only. | <u>, </u> |
| | • | | |

| TABLE 4(a): UATM 2006 Sampling Schedule for Mayville | | | | | | | |
|--|--------|------------|--------|------------|--------|------------|--------|
| 1 Qtr | | 2 Qtr | | 3 Qtr | | 4 Qtr | |
| Date | Sample | Date | Sample | Date | Sample | Date | Sample |
| 01/05/2006 | A,B | 04/05/2006 | Ad,B | 07/04/2006 | Ad,B | 10/02/2006 | Ad,B |
| 01/11/2006 | Ad,Bd | 04/11/2006 | A,B | 07/10/2006 | A,Bd | 10/08/2006 | A,B |
| 01/17/2006 | A,B | 04/17/2006 | A,B | 07/16/2006 | A,B | 10/14/2006 | A,B |
| 01/23/2006 | A,B | 04/23/2006 | A,B | 07/22/2006 | A,B | 10/20/2006 | A,B |
| 01/29/2006 | A,B | 04/29/2006 | A,B | 07/28/2006 | A,B | 10/26/2006 | A,B |
| 02/04/2006 | Ab,B | 05/05/2006 | Ab,B | 08/03/2006 | Ab,B | 11/01/2006 | Ab,B |
| 02/10/2006 | A,B | 05/11/2006 | A,Bd | 08/09/2006 | A,B | 11/07/2006 | A,Bd |
| 02/16/2006 | A,B | 05/17/2006 | A,B | 08/15/2006 | A,B | 11/13/2006 | A,B |
| 02/22/2006 | A,B | 05/23/2006 | A,B | 08/21/2006 | A,B | 11/19/2006 | A,B |
| 02/28/2006 | A,B | 05/29/2006 | A,B | 08/27/2006 | A,B | 11/25/2006 | A,B |
| 03/06/2006 | A,B,# | 06/04/2006 | A,B,# | 09/02/2006 | A,B,# | 12/01/2006 | A,B,# |
| 03/12/2006 | A,Bd | 06/10/2006 | A,B | 09/08/2006 | A,Bd | 12/07/2006 | A,B |
| 03/18/2006 | A,B | 06/16/2006 | A,B | 09/14/2006 | A,B | 12/13/2006 | A,B |
| 03/24/2006 | A,B | 06/22/2006 | A,B | 09/20/2006 | A,B | 12/19/2006 | A,B |
| 03/30/2006 | A,B | 06/28/2006 | A,B | 09/26/2006 | A,B | 12/25/2006 | A,B |
| | | | | | | 12/31/2006 | A,B |

- Sampling Schedule Code Key
 A Ambient sampling for VOCs and Carbonyls
 B Ambient sampling metals
 d duplicate sample
 b trip blank
 # one point flow check

| TABLE 4(b): UATM 2006 Sampling Schedule for Madison Site | | | | | | | |
|--|--------|------------|--------|------------|--------|------------|--------|
| 1 Qtr | | 2 Qt | r | 3 Qtr | | 4 Qtr | |
| Date | Sample | Date | Sample | Date | Sample | Date | Sample |
| 01/05/2006 | A | 04/05/2006 | A,B | 07/04/2006 | A | 10/02/2006 | A,B |
| 01/11/2006 | A,B | 04/11/2006 | A | 07/10/2006 | A,B | 10/08/2006 | A |
| 01/17/2006 | A | 04/17/2006 | A,B | 07/16/2006 | A | 10/14/2006 | A,B |
| 01/23/2006 | A,B | 04/23/2006 | Ab | 07/22/2006 | A,B | 10/20/2006 | Ab |
| 01/29/2006 | Ab | 04/29/2006 | A,B | 07/28/2006 | Ab | 10/26/2006 | A,B |
| 02/04/2006 | A,B,# | 05/05/2006 | A,# | 08/03/2006 | A,B,# | 11/01/2006 | A,# |
| 02/10/2006 | A | 05/11/2006 | A,B | 08/09/2006 | A | 11/07/2006 | A,B |
| 02/16/2006 | A,B | 05/17/2006 | A | 08/15/2006 | A,B | 11/13/2006 | A |
| 02/22/2006 | A | 05/23/2006 | A,B | 08/21/2006 | A | 11/19/2006 | A,B |
| 02/28/2006 | A,B | 05/29/2006 | A | 08/27/2006 | A,B | 11/25/2006 | A |
| 03/06/2006 | A | 06/04/2006 | A,B | 09/02/2006 | A | 12/01/2006 | A,B |
| 03/12/2006 | A,B | 06/10/2006 | A | 09/08/2006 | A,B | 12/07/2006 | A |
| 03/18/2006 | A | 06/16/2006 | A,B | 09/14/2006 | A | 12/13/2006 | A,B |
| 03/24/2006 | A,B | 06/22/2006 | A | 09/20/2006 | A,B | 12/19/2006 | A |
| 03/30/2006 | A | 06/28/2006 | A,B | 09/26/2006 | A | 12/25/2006 | A,B |
| | | | | | | 12/31/2006 | A |

Sampling Schedule Code Key

- $A-Ambient\ sampling\ for\ VOCs\ and\ Carbonyls$
- B Ambient sampling metals
- d duplicate sample
- $b-trip\ blank$
- # one point flow check

| TABLE 4(c): UATM 2006 Sampling Schedule for Milwaukee and Statewide Metals Sites | | | | | | | | |
|--|--------|------------|--------|------------|--------|------------|--------|--|
| 1 Qtr | | 2 Qtı | 2 Qtr | | 3 Qtr | | 4 Qtr | |
| Date | Sample | Date | Sample | Date | Sample | Date | Sample | |
| 01/05/2006 | Ad | 04/05/2006 | C | 07/04/2006 | Ad | 10/02/2006 | C | |
| 01/11/2006 | C | 04/11/2006 | Ad | 07/10/2006 | C | 10/08/2006 | A | |
| 01/17/2006 | A | 04/17/2006 | C | 07/16/2006 | A | 10/14/2006 | C | |
| 01/23/2006 | C,B | 04/23/2006 | A,B | 07/22/2006 | C,B | 10/20/2006 | A,B | |
| 01/29/2006 | Ab | 04/29/2006 | C | 07/28/2006 | Ab | 10/26/2006 | C | |
| 02/04/2006 | C | 05/05/2006 | Ab,# | 08/03/2006 | C | 11/01/2006 | Ab,# | |
| 02/10/2006 | A,# | 05/11/2006 | Cd | 08/09/2006 | A,# | 11/07/2006 | C | |
| 02/16/2006 | Cd | 05/17/2006 | A | 08/15/2006 | C | 11/13/2006 | A | |
| 02/22/2006 | A,B | 05/23/2006 | C,B | 08/21/2006 | A,B | 11/19/2006 | C,B | |
| 02/28/2006 | C | 05/29/2006 | A | 08/27/2006 | Cd | 11/25/2006 | A | |
| 03/06/2006 | A | 06/04/2006 | С,# | 09/02/2006 | A | 12/01/2006 | C | |
| 03/12/2006 | С,# | 06/10/2006 | A | 09/08/2006 | С,# | 12/07/2006 | A | |
| 03/18/2006 | A | 06/16/2006 | С | 09/14/2006 | A | 12/13/2006 | С,# | |
| 03/24/2006 | C,B | 06/22/2006 | A,B | 09/20/2006 | C,B | 12/19/2006 | A | |
| 03/30/2006 | A | 06/28/2006 | C | 09/26/2006 | A | 12/25/2006 | C,B | |
| | | | | | | 12/31/2006 | A | |

Sampling Schedule Code Key

A – Ambient sampling for VOCs and Carbonyls

B- Ambient sampling metals

C – Ambient sampling for PCBs

d – duplicate sample

b – trip blank

- one point flow check

Site Notes:

Milwaukee, Sixteenth Street Health Center site—all samples will be collected. This is the only site for PCB duplicates.

Forest County Potawatomi site – Only Metal samples will be collected.